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Studies in the Stereochemistry of Quinquevalent Nitrogen. III.

Autoracemisation of Optically Active Ammonium Compounds.

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Autoracemisation of optically active ammonium compounds was first observed by Pope and Harvey[1] with dextro methyl allyl phenyl benzyl ammonium iodide in its chloroform solution, and since then the study of its cause and mechanism has been attempted by many investigators, but the problem has not been solved yet.

It has been known that racemisation of ammonium compounds occurs almost always in the solvents of a small dielectric constant[2] such as chloroform, bromoform, carbon bisulphide and benzene, which stand in a close connection with the chemical nature of the atoms or atomic groups linked to the nitrogen atom[3], and again that the velocity of reaction is facilitated by tne influence of light and heat.[4]

The different hypothesis put forward by the different investigators, for the explanation of the mechanism of autracemisation will be stated below:

1. Permutation Theory.

H. Goldschmidt[5] is of an opinion that the racemisation of ammonium compounds may be caused by the permutation of the positions of atomic groups linked to the nitrogen within the molecule, as in the case of tautomeric change, and has proposed a following theoretical

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1 J. Chem. Soc., **91**, 828 (1901).

2 Jones: *Ibid*, **87**, 135 (1905); **89**, 281 (1906): Wedekind: Ber. D. Chem. Ges., **38**, 343, 3933 (1905); **39**, 478 (1906); Z. Eleck. Chem., **12**, 331 (1906): Halban: Ber. D. Chem. Ges., **41**, 2417 (1908).

3 Jones: J. Chem. Soc., **89**, 281 (1906); Wedekind and Paschke: Ber. D. Chem. Ges., **44**, 1406 (1911).

4 Pope: J. Chem. Soc., **75**, 1127 (1899); **79**, 828 (1901); Jones: *Ibid.*, **87**, 135 (1905); **89**, 281 (1906); Wedekind: Z. Phys. Chem., **45**, 242 (1903); Wedekind and Paschke: Ber. D. Chem. Ges., **41**, 1029 (1908); Halban: *Loc. cit.*

5 Z. Eleck. Chem., **12**, 416, 516 (1906); Le Bell: Compt. rend., **130**, 1552 (1900).

expression based upon a thermodynamical principle, explaining the mechanism of reaction:

$$A = 2RT\,ln\,2.$$

2. Dissociation Theory.

Pope[1], drawing a conclusion from his experimental results, has attributed the phenomena of racemisation to the dissociation of ammonium compounds into alkyl haloid and tertiary amine and to their subsequent recombination, resulting eventually in equilibrium with the formation of equal quantities of the dextro and lævo isomerides, as will be shown in the following scheme:

$$R^1R^2R^3R^4NI \rightleftarrows R^1R^2R^3N + R^4I$$

and he also declares that heat and light, and a basic radical attached to nitrogen atom such as an allyl or benzyl group have to promote the tendency of dissociation.

3. Decomposition Theory.

In the molecular weight determination of methyl allyl phenyl benzyl ammonium iodide in chloroform solution by the microscopic method, carried out by Barger,[2] Halban[3] has been induced to the notion that optically active ammonium compounds, decompose in their racemisation into tertiary amines and alkyl haloides as will be shown in the following scheme:

$$R^1R^2R^3R^4NI \longrightarrow R^1R^2R^3N + R^4I.$$

Such hypothesis has been confirmed by determining the amounts of ammonium salts remained without decomposition, in the chloroform solutions which decrease in proportion to the duration of time, by titration with the standard silver nitrate solution.

Wedekind,[4] also denies the dissociation and permutation theories and supports Halban's explanation inferring from the molecular weight determination by the cryoscopic method in a benzene solution, the conductivity measurement of the ammonium salt solutions and the comparative determination of their optical rotations.

Now, allowing a chloroform solution of methyl allyl phenyl ben-

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1 *Loc. cit.*

2 J. Chem. Soc., **85**, 315 (1904).

3 Z. Eleck. Chem., **13**, 57 (1907); Ber. D. Chem. Ges., **41**, 2417 (1908).

4 Ber. D. Chem., Ges., **41**, 2689 (1908); **44**, 1406, 3078 (1911).

zyl ammonium iodide, as observed by Wedekind and Paschke[1] to stand, it changed gradually yellow emitting the characteristic odour of benzyl iodide, and these facts seem to give a support to the decomposition theory by Halban. In order to determine the true nature of autoracemisation of optically active ammonium compounds, and if possible, to decide the cause of such a phenomenon the author has undertaken the present investigation.

I. Mechanism of the Autoracemisation.

For studying the nature of the reaction, the author has examined the velocity of the racemisation of the ammonium iodides in chloroform solutions at 25° with polarimeter, and calculated the velocity-constants as the monomolecular reaction by the following formula :

$$k = \frac{1}{t} \log \frac{a_0}{a} = \frac{1}{t} \log \frac{1}{1-x}$$

where a_0 denotes the initial rotatory power, a one at any time t and $x = \frac{a_0 - a}{a_0}$.

As seen in the experimental results shown in the tables I, II, IV and V, the velocity constants of α and γ dextro methyl allyl phenyl benzyl ammonium iodides are same, and also coincide with those observed by Wedekind[2] by the same method, but not with Halban's observation.[3] Further, the constant of dextro methyl *n*-propyl phenyl benzyl ammonium iodide was found to be same with that of Wedekind.[4]

Inferring the nature of racemisation from the reaction velocity it may belong to an intramolecular reaction[5] which is considered as a self-decomposition or dissociation of molecule. The fact that the racemisation constants of α and γ dextro methyl allyl phenyl benzyl ammonium iodides in chloroform solution are identical, while their specific rotations are different, would furnish a support to the decomposition theory.

For the confirmation of such a view, the author has examined the absorption spectra, in the ultraviolet rays, of a chloroform solution

1 Ber. D. Chem. Ges **43**, 1303 (1910).
2 Z. Eleck. Chem., **12**, 332 (1906); Ber. D. Chem. Ges., **41**, 1029 (1908).
3 Z. Elect. Chem., **13**, 57 (1907).
4 Ber. D. Chem. Ges., **41**, 2659 (1908).
5 E. Wedekind: Die Entwicklung der Stereochemie des fünfwertigen Stickstoffs in letzten Jahrzehnt, 1909. s 33.

of freshly prepared dextro methyl allyl phenyl benzyl ammonium iodide, the same solution which has been allowed to stand for a day and a solution of methyl allyl aniline which is supposed as one of the decomposition products of the above iodide, all under the same condition, and actually the results of experiment, as shown in Fig. 1, seem to realise our view.

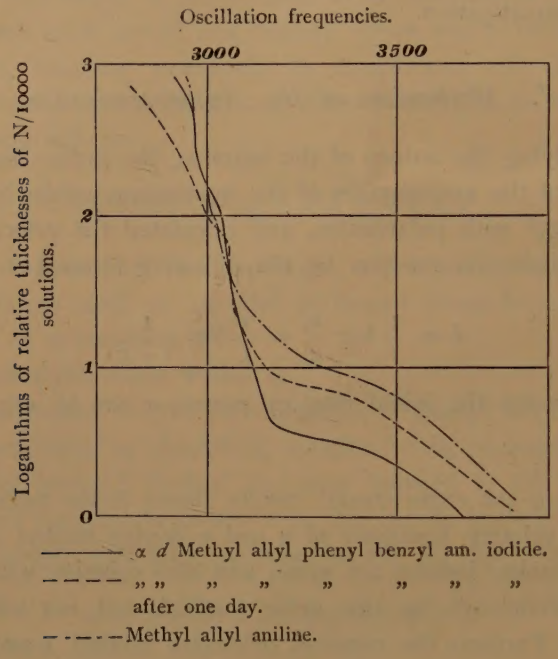


Fig. 1.

Theoretically it may be assured that when substance AB dissociates into A and B there may still exist a kind of chemical affinity between them on account of their reversibility, being different from decomposition :

$$AB \rightleftarrows A^{+} + B^{-} \text{ (Dissociation)}$$

$$AB \longrightarrow A + B \text{ (Decomposition)}$$

Now extending the above view for the racemisation of ammonium compounds and taking an account the decomposition phenomena of the ammonium bases by heat[1] for the consideration, it is highly

1 Mem. Colli. Sci. Engin., Kyoto. 3, 371 (1912).

probable that when α and γ dextro methyl allyl phenyl benzyl ammonium iodides are dissolved in chloroform, each gradually decomposes into methyl allyl aniline and benzyl iodide, and the decomposition products, in a greater part, recombine to the same ammonium iodide, that is, γ methyl allyl phenyl benzyl ammonium iodide, respectively.

$$\alpha \text{ and } \gamma\ d\,R^1R^2R^3R^4NI \longrightarrow R^1R^2R^3N + R^4I \longrightarrow \gamma r\,R^1R^2R^3R^1NI.$$

When a chloroform solution of α methyl allyl phenyl benzyl ammonium iodide was set aside for 3 days in a laboratory, it changed orange yellow in colour, and after distilling off the solvent there was found to remain a brownish orange viscous residue which on standing for a few days produced a crystalline mass consisting of methyl allyl phenyl benzyl ammonium iodide. The substance thus formed was made to crystallize from alcohol and subjected to resolution with anhydrous silver camphorsulphonate as usual. The reaction product recrystallized from acetone was observed to show $[2]_D^{25} = +51{\cdot}0°$ for its specific rotatory power in an aqueous solution.

In the second experiment, α methyl allyl phenyl benzyl ammonium iodide was heated to boil in chloroform solution at 62° for 2 days, and a dark brown syrupy substance obtained from the solution was confirmed to consist of methyl allyl aniline and benzyl iodide.

Pure methyl allyl phenyl benzyl ammonium iodide isolated from the above dark brown syrupy substance was mesotomized with silver dextro-camphorsulphonate into two optical antipodes, and the purified dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate melting at 162–163°, gave the same specific rotatory power $[\alpha]_D^{25} = +56{\cdot}48°$ as that of γ isomeride.

In the third experiment, the raw dextro methyl allyl phenyl benzyl ammonium iodide heated to boil in its chloroform solution at 62° for 3 days, was converted into racemic ammonium iodide which was identified after resolution, by its rotatory power of camphorsulphonate.

On the other hand the author has treated the γ inactive isomeride under the same conditions as in α isomer, and found that pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, thus formed, has the same melting point and specific rotatory power in its aqueous solution as in the active γ compound.

Hence, we may conclude that the primary cause in the autoracemisation of the optically active ammonium iodide in a chloroform solu-

tion would be ascribed to the decomposition of the compound into tertiary amine and alkyl iodide: subsequently the formation of the inactive ammonium iodide would take place, and the mechanism of the reaction may be represented as in the scheme already shown.

II. Cause of Autoracemisation of Optically Active Ammonium Compounds.

As a matter of fact, the autoracemisation of optically active ammonium compounds takes place in a solvent of small dielectric constant, but there is found no precise relation to exist between the reaction velocity in a solvent and its dielectric constant and also between the reaction velocity of the substance and its solubility in a solvent.

Since the reaction actually takes place in a medium containing a halogen, it was supposed that the reaction may be caused by the catalytic action of halogen-acid generated by self decomposition of a solvent or of some other impurities which may come from the solvent during preservation.[1]

For this problem, the racemisation velocity of *a* dextro methyl allyl phenyl benzyl ammonium iodide in three kinds of chloroform solution, that is, in the purified chloroform kept for just one year in a dark cold place, in the freshly distilled chloroform and in the latter containing N/2000 HCl, was examined under the same conditions.

As seen in the results shown in the tables I, II, IV and VII, the impurity in chloroform exerts no remarkable influence upon the velocity of racemisation; in other words, the primary cause of the reaction should be ascribed to the action of the solvent itself but not to the catalytic action of halogen acid or some other impurities present in medium.

It was noticed by the author that optically active methyl *n*-prophyl phenyl benzyl ammonium iodide in the allyl alcohol and acetonitrile solutions slowly lessened its rotatory power on standing, and moreover, though the rotatory power of the substance in ethyl alcohol solution did not change when left for three days in a tube carrying metallic mantel preventing the action of light, but in alcohol containing carbon tetrachloride, chlorobenzene, acetylen dichloride, amylene and cro-

[1] P. Walden: Ber. D. Chem. Ges., **31**, 1422 (1898).

tonic acid, as seen in the experimental part the racemisation took place gradually.

From the experimental data, the author calculated approximately the time in which the half of the initial rotatory power of the active substance has been diminished, and from which the author have to compare the actions of solvents on the racemisation.

Solvents.	Time (in hours).
Chloroform Cl_3CH.	3
Amylene $CH_3CH_2CH=CHCH_3$	3
Chlorobenzene $Cl.C_6H_5$.	48
Carbon tetrachloride CCl_4	49
Acetylen dichloride $CHCl=CHCl$	52
Acetonirile CH_3CN	53
Crotonic acid $CH_3CH=CHCO_2H$	58
Allyl alcohol $CH_2=CHCH_2OH$	119

These facts have induced the author to the notion that the decomposition of optically active substances would be caused by the common force which might exist in those solvents, and the author have to designate it as a residual affinity of solvents which may be due to the presence of a polyvalent element or unsaturated linking in molecule.

III. Thermal Effect in Optically Active Ammonium Compounds.

By thermal analysis, the author has intended to study the chemical change of optically active compounds in the fused state.

When α methyl allyl phenyl benzyl ammonium iodide in a fine powder was gradually heated in a tube over a sulphuric acid bath, the reading of thermometer which was inserted into the substance was observed to depress for a few degrees from 120° with the active substance, while with the racemic one from 105°.

It will be indicate that at these temperature the substances began to decompose.

Now the cooling curves for these substances have been plotted according to Tanmann's method which is applied to the investigation of alloys, and the results are shown in Fig. 2.

According to the author's investigation which is expected to be communicated in a near future we can imagine that a chemical change of a substance may occur in fusion being inferred from its cooling curve, and in the present case, it seems to the author that the substance have perfectly been decomposed into tertiary amine and alkyl iodide.

By chemically testing the fused mass, the presence of methyl allyl aniline and benzyl iodide was ascertained; consequently the author's assumption deduced from the cooling curve was realized.

Allowing the fused mass of a active substance to stand for a few days, methyl allyl phenyl benzyl ammonium iodide was obtained, which when purified by recrystallisation from alcohol, was confirmed to be inactive by polariscopic measurement.

Hence, the following conclusions may be drawn, when α dextro methyl allyl phenyl benzyl ammonium iodide is heated, it decomposes at about 120°, and in the fused state it splits up into methyl allyl aniline and benzyl iodide, which on standing recombine together forming inactive γ methyl allyl phenyl benzyl ammonium iodide as in the case with its chloroform solution.

EXPERIMENTAL PART.

Certain quantities of optically active ammonium compounds were dissolved in chloroform, and the solutions made up to 25 c.c. at constant temperature, and kept in a thermostat; each solution was taken in a 20 cm. glass tube of a polariscope which carries a metallic mantel to protect the action of light, and the observation of the angle of rotation conducted with sodium light.

In the experiments, the polarimeter tube was kept at a definite temperature, by letting the water of thermostat circulate through the mantel

The constant of the reaction-velocity was calculated by the formula of a monomolecular reaction.

1. 0·1232 grm. γ dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. chloroform which after purification had been kept for one year at a dark and cold place in the laboratory, and the rotatory power was observed at 25°, and the results are shown in the table I.

TABLE I.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·68°	—	—	—
25	0·64	0·0588	0·9412	0·0011
53	0·59	0·1324	0·8676	0·0012
86	0·50	0·2647	0·7353	0·0015
153	0·32	0·5294	0·4706	0·0022
223	0·26	0·6176	0·3824	0·0019
275	0·21	0·6912	0·3088	0·0018
343	0·11	0·8382	0·1618	0·0022
			Mean	0·0017

2. 0·1624 grm. of the same substance was dissolved in the same solvent as above, and its velocity of racemisation was determined at 30°.

TABLE II.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·77°	—	—	—
60	0·50	0·3506	0·6494	0·0031
125	0·20	0·7403	0·2597	0·0046
165	0·2	0·9740	0·0260	0·0035
			Mean	0·0038

From the Table I and II, the temperature coefficient of racemisation has been calculated as 4·5.

3. 0·1327 grm. γ lævo methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform and its velocity of the reaction was observed at 25°, and the results are shown in the table III.

TABLE III.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·51°	—	—	—
36	0·47	0·0784	0·9216	0·0010
86	0·37	0·2745	0·7255	0·0016
128	0·33	0·3530	0·6470	0·0015
221	0·29	0·4314	0·5686	0·0011

250	0·22	0·5295	0·4705	0·0014
346	0·14	0·7255	0·2745	0·0016
			Mean	0·0014

The velocity-constant at 25° is same with that of the antipode observed at the same temperature.

4. 0·1264 grm. *α* dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform above mentioned, and its velocity of racemisation was determined at 25°.

TABLE IV.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·39°	—	—	—
22	0·36	0·0769	0·9231	0·0015
52	0·30	0·2308	0·7692	0·0022
182	0·17	0·5641	0·4359	0·0019
			Mean	0·0019

5. 0.228 grm. *α* dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform, and its velocity of racemisation was observed at 30°. The results of the experiments are shown in the following table V.

TABLE V.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·90°	—	—	—
30	0·78	0·1333	0·8667	0·0021
82	0·57	0·3666	0·6334	0·0024
160	0·41	0·5444	0·4556	0·0021
225	0·25	0·7222	0·2778	0·0025
295	0·17	0·8111	0·1889	0·0025
			Mean	0·0023

As it was assumed that the impurities which may come from the solvents by decomposition or from some other unknown reactions

which is possible to take place during their preservation, might exert some influence upon racemisation, the following experiments were carried out by using the chloroform purified by distillation, after treating it with water and sulphuric acid successibely.

6. 0.2245 grm. *α* dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. the purified chloroform, and its velocity of reaction was determined at 25°.

TABLE VI.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·95°	—	—	—
95	0·75	0·2105	0·7895	0·0011
160	0·60	0·3684	0·6316	0·0012
215	0·46	0·5158	0·4842	0·0014
270	0·35	0·6316	0·3584	0·0015
343	0·21	0·7790	0·2210	0·0019
			Mean	0·0014

7. 0·227 grm. of the substance was dissolved in 25 c.c. of chloroform containing N/2000 hydrochloric acid, and its velocity of racemisation was determined at 25°.

TABLE VII.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	0·91°	—	—	—
52	0·80	0·1209	0·8791	0·0011
143	0·63	0·3077	0·6923	0·0011
195	0·56	0·3846	0·6154	0·0011
260	0·37	0·5934	0·4066	0·0015
380	0·34	0·6264	0·3736	0·0011
			Mean	0·0012

8. 0.2062 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in chloroform and the solution made up to 25 c.c. with chloroform and its velocity of reaction was observed at 25°.

The results as will be shown in the following table, is identical with that obtained by Wedekind.[1]

[1] *Loc. cit.*

Table VIII.

t (in minutes)	α	x	$1-x$	$k=\frac{1}{t}\log\frac{1}{1-x}$.
0	1·44°	—	—	—
60	1·25	0·1320	0·8680	0·0010
117	1·00	0·3056	0·6944	0·0014
175	0·77	0·4653	0·5347	0·0016
225	0·58	0·5972	0·4028	0·0017
302	0·43	0·7012	0·2988	0·0017
380	0·24	0·8333	0·1667	0·0020
				Mean 0·0016

9. 0·172 grm. *α* dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. allyl alcohol from Kahlbaum, and the velocity of racemisation was observed at 25°.

Table IX.

t (in hours)	0	81	119
α	0·79°	0·44	0·39

10. 0·131 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. acetonitrile from Kahlbaum, and the racemisation-velocity was observed at 25°. The results will be shown in the following table.

Table X.

t (in hours)	0	1	6	28	42
α	0·70°	0·67	0·55	0·50	0·42

11. 0·1192 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol containing 10 c.c. amylene form Kahlbaum and the solution made up to 50 c.c. with alcohol at 25°, and the racemisation-velocity measured at 25°. When amylene was added to alcoholic solution of the substance, the solution was found to colour instantly yellowish orange.

Table XI.

t (in minutes)	0	85	170
α	0·38°	0·28	0·20

12. 0·083 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide and 5 grm. *a*-crotonic acid from Kahlbaum were dissolved in 25 c.c. alcohol and the racemisation-velocity was examined with such solution. The results will be shown in the table XII.

t (in hours)	0	2	7	58
α	0·58°	0·48	0·45	0·40

13. Lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol containing 5 c.c. butyric acid and the solution made up to 25 c.c. with alcohol, and the angle of rotation of the solution was examined at 25°. It was observed that after 2 days the angle of the rotation of the solution was kept constant at $\alpha_D = -0{\cdot}25°$

14. 0·0595 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol, containing 5 c.c. carbon tetrachloride from Kahlbaum, and the solution made up to 25 c.c. with alcohol. The velocity of racemisation was observed at 25°.

TABLE XIV.

t (in hours)	0	4	9	32
α	0·45°	0·42	0·35	0·30

15. 0·077 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol, containing 5 c.c. acetylene dichloride and the solution made up to 25 c.c. with alcohol, and the racemisation-velocity of the solution was observed at 25°.

TABLE XV.

t (in hours)	0	9	27
α	0·40°	0·35	0·29

16. Lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in a mixture of 40 c.c. alcohol and 10 c.c. chlorobenzene from Kahlbaum, and the racemisation-velocity of the solution was observed.

TABLE XVI.

t (in hours)	0	51	123
α	0·22°	0·20	0·5

17. Chemical Change of α Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide in the Chloroform Solution.

A. Pure *α* methyl allyl phenyl benzyl ammonium iodide was resolved into its optically active components by means of silver dextro-camphorsulphonate.

α Dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate recrystallized from acetone 5 times, was found to melt at 162° and its rotatory power in an aqueous solution was determined.

A solution of 0·2159 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}0°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +46{\cdot}54°$.

A solution of 0·4535 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}67°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +46{\cdot}03°$.

B. 7 grm. pure *α* ammonium iodide above mentioned was dissolved in 150 c.cm. chloroform from Kahlbaum, and the solution was left to stand for 3 days in the laboratory, during which time its colour changed yellowish orange.

After distilling off the solvent, there was left a dark brownish orange syrupy residue from which pure methyl allyl phenyl benzyl ammonium iodide was isolated, and its yield was found to be 3·5 grm. The melting point of the substance was noticed to be 127–128°.

3·5 grm. the iodide and 3·5 grm. silver camphorsulphonate were mixed in acetone-acetic ester, and the mixture treated as usual.

Pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate crystallized from acetone 4 times, possesses the melting point 165–166°, and the same physical and chemical properties as those of the active *α* compound.

A solution of 0·2792 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +1{\cdot}14°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +51{\cdot}04°$.

C. 20 grm. pure *α* methyl allyl phenyl benzyl ammonium iodide was heated, dissolved in 300 c.c. chloroform at 62° for one day. After such a treatment, the solvent was distilled off and a part of the residue treated with ether to dissolve the decomposition products contained in it. From the etherial solution, methyl allyl aniline and benzyl iodide were obtained, and the latter was identified by converting into benzaldehyde by oxidation with copper nitrate.

Methyl allyl aniline was analysed by changing it into ferrocyanide, and the result was as follows:

0·115 grm. amine ferrocyanide gave 0·0205 grm. Fe_2O_3 on ignition.

	Calc. for $C_{26}H_{30}N_8Fe$.	Found.
Iron	10·96	12·54

Another part of the residue was allowed to stand, solidifiing in a crystalline mass from which 6 grm. pure methyl allyl phenyl benzyl ammonium iodide were obtained and its melting point was found to be 125–126°.

6 grm. pure iodide was mesotomized with 6 grm. silver dextro camphorsulphonate in the acetone-ethyl acetate solution. The reaction product was mercerized with acetone 3 times and once with ethyl acetate. *α* Dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, thus obtained, consisted of fine needle-shaped crystals melting at 162–163° and its yield was found to be 0·2 grm.

The rotatory power of the aqueous solution was determined and the result will be mentioned in the following statements:

A solution of 0·14 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0.66°$ in a 20 cm. tube, whence $[\alpha]_D^{25} = +58·93°$.

Dextro methyl allyl phenyl benzyl ammonium iodide obtained from the above camphorsulphonate, crystallizes from ethyl alcohol in fine white needles which melt at 133–134°.

A solution of 0·0513 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0·28°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +68·23°$.

D. 10 grm. crude *α* dextro methyl allyl phenyl benzyl ammonium iodide was kept to boil in the chloroform solution at 62° for 3 days on a water bath. Letting the syrupy residue for 5 days stand, it solidified to a crystalline mass, from which 3 grm. methyl allyl phenyl benzyl ammonium iodide was isolated.

3 grm. of the iodide was treated with 3 grm. silver camphorsulphonate in acetone-ethyl acetate solution as usual. The reaction product was made to recrystallize from acetone 4 times and ethyl acetate 2 times successively, and dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate melting at 162–163° was obtained in fine colourless needles, and its yield was found to be about 0·18 grm.

A solution of 0·156 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}74°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +58{\cdot}75°$.

Dextro methyl allyl phenyl benzyl ammonium iodide obtained by adding potassium iodide to the aqueous solution of the camphorsulphonate above mentioned, was found to melt at 133–134°.

A solution of 0·061 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}31°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +63{\cdot}52°$.

18. *Chemical Change of γ Methyl Allyl Phenyl Benzyl Ammonium Iodide in the Chloroform Solution.*

γ Methyl allyl phenyl benzyl ammonium iodide was heated in chloroform solution at 62° for one day, and the solution treated in the same manner as in α compound.

5 grm. methyl allyl phenyl benzyl ammonium iodide, thus obtained was treated with 5 grm. silver dextro camphorsulphonate in acetone-ethyl acetate solution.

The reaction product was made to recrystallize from acetone 2 times and ethyl acetate once.

Dextro methyl allyl phenyl benzyl ammonium dextrocamphorsulphonate consists of fine colourless needles melting at 161–162°, and its yield was found to be 0·18 grm.

A solution 0·1784 grm. substance made up to 25 c.c. with water at 25°, gave $\alpha_D^{25} = +0{\cdot}80°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +56{\cdot}06°$.

Dextro methyl allyl phenyl benzyl ammonium iodide obtained from camphorsulphonate above mentioned, crystallizes from alcohol in white needles; its rotatory power was determined in a alcoholic solution.

A solution of 0·0875 grm. substance made up to 25 c.c. with alcohol at 25°, gave $\alpha_D^{25} = +0{\cdot}44°$ in a 20 cm. tube; whence $[\alpha]_D^{25} = +65{\cdot}71°$

19. *Experiment on the Fused α Methyl Allyl Phenyl Benzyl Ammonium Iodide.*

A. When 0·7 grm. pure α dextro methyl allyl phenyl benzyl ammonium iodide (its specific rotatory power in alcoholic solution is $[\alpha]_D^{25} = +52{\cdot}38°$) made in a fine powder, was gradually heated in a Jena-glass tube of 8 mm in diameter on a double walled sulphuric acid bath, it changed yellow at 115°, and at 124° the height of the

thermometer inserted into the substance ceased to rise for 20 seconds, and then it changed to an orange red fluid perfectly at 144°.

The cooling velocity of the fused mass was observed, and a curve was plotted with the times and temperatures. The result will be shown in Fig. 2 (denoted in a dotted line). Allowing it to stand for 2 days it solidified to a crystalline mass, from which methyl allyl phenyl benzyl ammonium iodide was isolated.

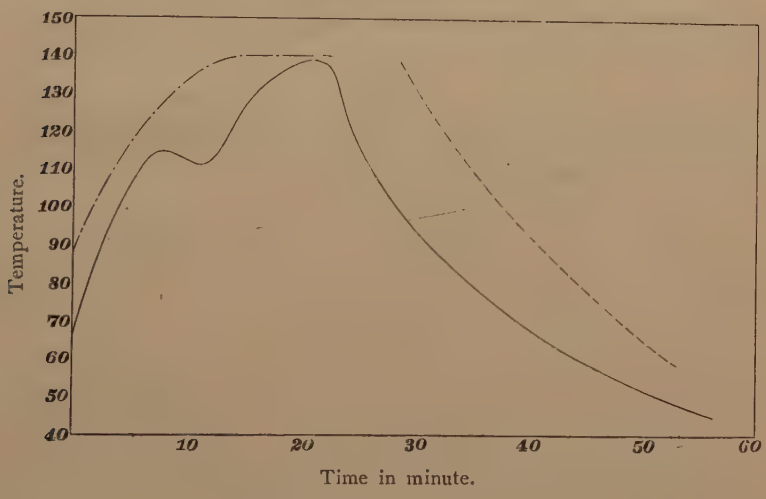


Fig. 2.

The substance recrystallized from alcohol, melted at 125–126°, its alcoholic solution having been observed to be inactive.

B. 3 grm. pure methyl allyl phenyl benzyl ammonium iodide was heated under the same condition as for the active compound, but it was observed to decompose at about 114·5°

The thermal change of the substance and the rate of cooling of the fused mass, was plotted as shown in Fig. 2 (in a thick line).

By treating the fused mass with ether, it was almost entirely dissolved leaving a trace of reddish brown mass. The etherial solution was treated with dilute hydrochloric acid, and from the upper layer of the solution, benzyl iodide was isolated, which was converted into benzaldehyde by oxidation with copper nitrate and the aldehyde was identified by its phenylhydrazone (mp. 152°) and also by its odour.

The acidic lower layer of the solution was neutralized with caustic soda and extracted with ether. Evaporating the ether, there remained an yellow oil which was confirmed to be methyl allyl aniline by analysis of its ferrocyanide and by the melting point of the picrate.

0·10 grm. the ferrocyanide gave 0·0158 grm. Fe_2O_3 on ignition.

	Calc. for $C_{26}H_{39}N_8Fe$.	Found.
Iron	10·96	11·08

Allowing the fused mass of the iodide to stand for 3 days, it solidified to a crystalline mass from which pure methyl allyl phenyl benzyl ammonium iodide was isolated. The substance melts at 123–124°, and by analysis gave the following results:

0·104 grm. substance gave 0·067 grm. AgI.

	Calc. for $C_{16}H_{20}NI$	Found.
Iodine	34·79	34·82

On the System: Sodium Sulphate—Sodium Chromate—Water.

By

Isakichi Takeuchi.

(Received May 15, 1915.)

It is a familiar fact that there exist mixed crystals between sodium sulphate and sodium chromate; but no systematic study from the stand point of the phase rule has yet been published.

Sodium chromate forms three hydrates, namely, deca-, hexa- and tetrahydrates, of which the first is isomorphous with the decahydrate of sodium sulphate. A few data given by T. W. Richards[1] refer to the relative composition of mixed crystals of decahydrates and mother liquor. The present article is an account of the result of a study on the equilibriums of the system at 15·0° and 25·0°.

Materials: Pure crystallised sodium sulphate, of E. Merck, was recrystallised as $Na_2SO_4.10H_2O$. Sodium chromate neutral, of the same factory, was three times recrystallised as decahydrate $Na_2CrO_4.10H_2O$, which was found to contain no other impurities than sodium sulphate. On standing its supersaturated solution at about 20° for crystallisation, hexahydrate $Na_2CrO_4.6H_2O$ was prepared. As the crystals thus obtained contained a small quantity of sodium sulphate, pure salt, prepared by neutralizing sodium bichromate with pure sodium hydroxide after the method proposed by Richards[2], was used whereat the content of sodium chromate amounted to 95 per cent or more. Ordinary distilled water was used.

Method of Experiment: Mixtures of the three substances in different proportions were put each in an Erlenmeyer flask of capacity of about 30 cc. which was made to rotate in a thermostat. After one or two days when the equilibrium would have been attained, the content was filtered through cotton wool or filter paper to separate the saturated solution from the residue, filtration being carried out by means

1 J. Am. Chem. Soc., **33**, 855 (1911).

2 *loc. cit.*, 849.

of a funnel and a receiver which had been immersed in the same thermostat. In order to remove the adhering mother liquor from the residue, the latter was pressed between folded filter paper previously warmed to about the same temperature as that of the thermostat.

Method of Analysis: Chromate was estimated by the ordinary method of iodimetry. Sulphate was determined as barium sulphate after reducing the chromate to the chromic salt with hydrochloric acid and alcohol. The precipitation of barium sulphate produced in this way was not always quite free from chromic salt, but the latter did not considerably affect the result. The residue was heated in a hard glass tube drawn out upward at both ends[1] at 150°–200° and the water, which might be contained as water of crystallisation, driven off. The amounts of water in the residue and in the solution were both found by subtraction. It was impossible to remove perfectly the adhering mother liquor from the residue, and consequently it had sometimes to be determined graphically by extraporation.

The results were as follows:

TABLE I.

Temperature: 15·0°.

No.	Composition of solution in gram percentage.			Composition of residue in gram percentage.		
	Na_2CrO_4	Na_2SO_4	H_2O	Na_2CrO_4	Na_2SO_4	H_2O
1	0	11·70	88·30	0	44·08	55·92
2	2·42	10·58	87·00	0·66	42·29	57·05
3	3·92	10·08	86·00	1·25	41·90	56·85
4	6·72	9·24	84·04	1·95	40·89	57·16
5	8·91	8·35	82·74	2·68	40·97	56·35
6	11·51	7·57	80·92	3·96	39·41	56·63
7	14·90	6·41	78·69	6·12	37·71	56·17
8	15·14	6·43	78·43	6.63	37·15	56·22
9	20·03	5·05	74·92	10·96	33·15	55·89
10	22·83	4·33	72·84	13·60	30·72	55·68
11	24 21	4·23	71·56	15·94	29·04	55·02
12	26·06	3·78	70·16	18·78	25·77	55·45

[1] See Ostwald-Luther, Physiko-Chemische Messungen., 3 Aufl., 264.

No.	Composing of solution in gram percentage.			Composition of residue in gram percentage.		
	Na_2CrO_4	Na_2SO_4	O_2H	Na_2CrO_4	Na_2SO_4	H_2O
13	28·49	3·18	69·33	22·89	22·37	54·74
14	31·34	2·32	66·34	29·03	16·39	54·58
15	33·34	1·55	65·11	35·48	10·71	53·81
16	33·90	1·31	64·79	38·62	7·49	53·89
17	36·44	0·47	63·09	43·66	2·96	53·38
18	37·17	0·24	62·59	46·06	1·06	52·88
19	37·45	0	62·55	47·35	0	52·65

If we take the formula $100m\ H_2O.xNa_2C_1O_4.(100-x)Na_2SO_4$ to represent the compositions of the solution and of the residue, the last table gives the following:

TABLE II.

No.	Solution.		Residue.	
	x	m	x	m
1	0	59·5	0	10·0
2	16·69	54·0	1·35	10·5
3	25·42	50·2	2·54	10·4
4	38·94	43·8	4·03	10 6
5	48·32	40·4	5·41	10·2
6	57·18	36·1	8·11	10·4
7	67·07	31·9	12·46	10·3
8	67·36	31·4	13·55	10·3
9	77·66	26·1	22·48	10·3
10	82·22	23·6	27·96	10·3
11	83·37	22·2	32·48	10·1
12	85.81	20·8	39·52	10·5
13	88·71	19·1	47·28	10·2
14	92·22	17·6	60·84	10·3
15	94·98	16·7	74·40	10·2
16	95·80	16·5	81·90	10·3
17	98·56	15·4	92·83	10·2
18	19·27	15·0	97·44	10·1
19	100·00	15·0	100·00	10·0

The corresponding tables for the other temperature are as follows :

TABLE III.

Temperature : 25·0°.

No.	Composition of solution in gram percentage.			Composition of residue in gram percentage.		
	Na_2CrO_4	Na_2SO_4	H_2O	Na_2CrO_4	Na_2SO_4	H_2O
1	0	21·90	78·10	0	44·08	55·92
2	1·56	20·76	77 68	0·55	42·85	56·60
3	2·53	20·12	77·35	0·82	43.48	55·70
4	4·02	18·96	77·02	1·22	42·03	56·75
5	4·95	18·62	76·43	1 29	43·09	55·62
6	9·66	16·49	73·85	2·91	41·02	56·07
7	14·19	14·71	71·10	4·49	39·56	55·95
8	14·85	13·87	71·28	4·18	39·36	56·46
9	16·22	13·91	69·87	5·72	38·46	55·82
10	23·72	10·69	65·59	9·22	37·00	53 78
11	26·13	10·02	63·85	12·51	32.35	55·14
12	31·70	8·32	59·98	16·11	30·01	53·88
13	31·43	8·49	60 08	15·59	34·08	50·33
14	31·84	8·63	59·53	12·86	54·14	33·00
15	32·34	8·03	59·63	5·71	85·81	8·48
16	34·75	6·75	58·50	5·94	84·35	9·71
17	38·59	4·44	56·97	5 70	86·94	7·36
18	39·22	4·38	56·40	8·83	79·22	11·95
19	42·48	2·79	54·73	13·27	72·66	14·07
20	43·80	2·20	54·00	25·50	56·72	17·78
21	43·83	2·29	53·88	48·54	18·21	33·25
22	43·26	2·44	54·30	58·18	3·45	38·37
23	43·57	2·18	54 25	53·85	10·59	35·56
24	43·69	2·12	54·19	53·89	8·78	37·33
25	43·49	2·24	54·27	57·93	2·10	39·97
26	43·53	2·20	54·27	58·50	1·47	40·03
27	44·61	1·08	54·31	59·17	0·38	40·45
28	45·76	0	54·24	59·75	0	40·25

TABLE IV.

No.	Solution.		Residue.	
	x	m	x	m
1	0	28·1	0	10 0
2	6·19	27·7	1·11	10·3
3	9·94	27·3	1·62	9·9
4	15 68	27·0	2·48	10·4
5	18·93	26·2	2·55	9 9
6	33·93	23·3	5·85	10·2
7	45·70	21·3	9·06	10·0
8	48·43	20·9	8·53	10 4
9	50·57	19·6	11·56	10·1
10	66·12	16·4	17 92	9·41
11	69.57	15·3	25·33	10 0
12	76·97	13·1	32·00	9·64
13	76·44	13·2	28·63	8·31
14	76·39	12·8	17·23	4·00
15	77·95	12·9	5·52	0 74
16	81·87	12·4	5·82	0·86
17	88·40	11·7	5·44	0 62
18	88·71	11·5	8·90	1·08
19	93·06	10.8	13·81	1·32
20	94·57	10·5	28·27	1·77
21	94 41	10·4	76·03	4·31
22	93 96	10·6	93·67	5·55
23	94·60	10·6	81·67	4 85
24	94·76	10 6	84·32	5·25
25	94·46	10 6	96·03	5·96
26	94·55	10.6	97·23	5·98
27	97·30	10·7	99·29	6·14
28	100·00	10·6	100·00	6·00

The data in Tables II and IV are diagrammatically shown in Fig. 1 and Fig. 2 respectively, taking m as ordinates and x as abscissas.

From Fig. 1, it is seen that decahydrates of sodium chromate and sodium sulphate are mutually miscible in all proportions at 15·0°. The solubility curve, however, has a point of inflection from which we can suspect some discontinuity in the residue, probably at the point,

x = ca. 33, and this becomes conspicuous in the results at the other temperature.

From Fig. 2 it is clear that the solubility curve at 25·0° consists of three branches. The solutions represented by the first branch AB are in equilibrium with decahydrated mixed crystals which are represented by the points in the horizontal $a\,b$, b denoting the limiting composition of the mixed crystals. Thus the range of existence of mixed crystals at 25·0° is from 0 to about 34 mol. per cent of the chromate. When more chromate is added to the system, the mixed crystals are decomposed and give rise to the anhydrous sulphate, the composition of the solution remaining constant at B so long as the mixed crystals still remain. The solutions represented by the second branch BC are in equilibrium with anhydrous sulphate as the residue In these cases the residue was a very fine powder and revealed its crystalline state only under a microscope, so that the adhering mother liquor could not be completely removed and this fact caused a somewhat remarkable error in the result. But in Fig. 2 the tie lines which connect the points in BC and their corresponding points representing the residues pass almost through the origin which represents anhydrous sodium sulphate, and, consequently, this salt must form the residue in those solutions.

The third branch of the solubility curve intersects with the second at C. One of the two solid phases with which the solution C is in equilibrium is obviously anhydrous sodium sulphate, the other is very likely pure hexahydrated chromate, since the straight line connecting the points representing anhydrous sulphate and pure hexahydrate passes through almost all the points which represent the residues with which the solution C is in equilibrium. Thus it seems that the hexahydrated sodium chromate does not form mixed crystals with the sulphate at 25·0°.

The point b which represents the limit of miscibility in the crystals is determined in Fig. 2 by the intersection of the straight line representing the residues which are in equilibrium with the solution B and the horizontal line representing ten mols of water. Within the limit of the error of the extrapolation, the composition of b is in good coincidence with that of a double salt $2Na_2SO_4.Na_2CrO_4.30H_2O$. But further investigations are required for the conclusion of the existence of the double salt and to my regret, time has not allowed me the solution of the question.

To Prof. Y. Osaka, at whose suggestion this work was undertaken, the auther wishes to express sincere thanks for his interest and advice.

Fig. 1.

Temperature : 15.°0

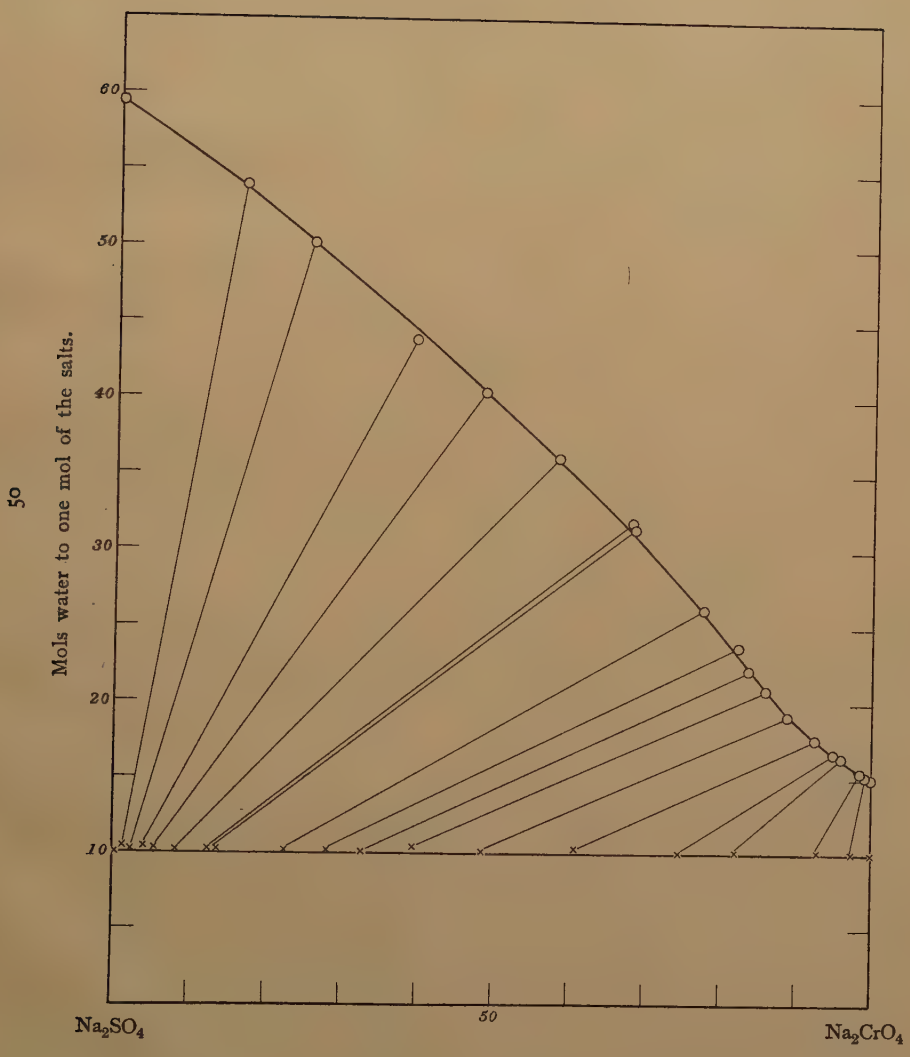
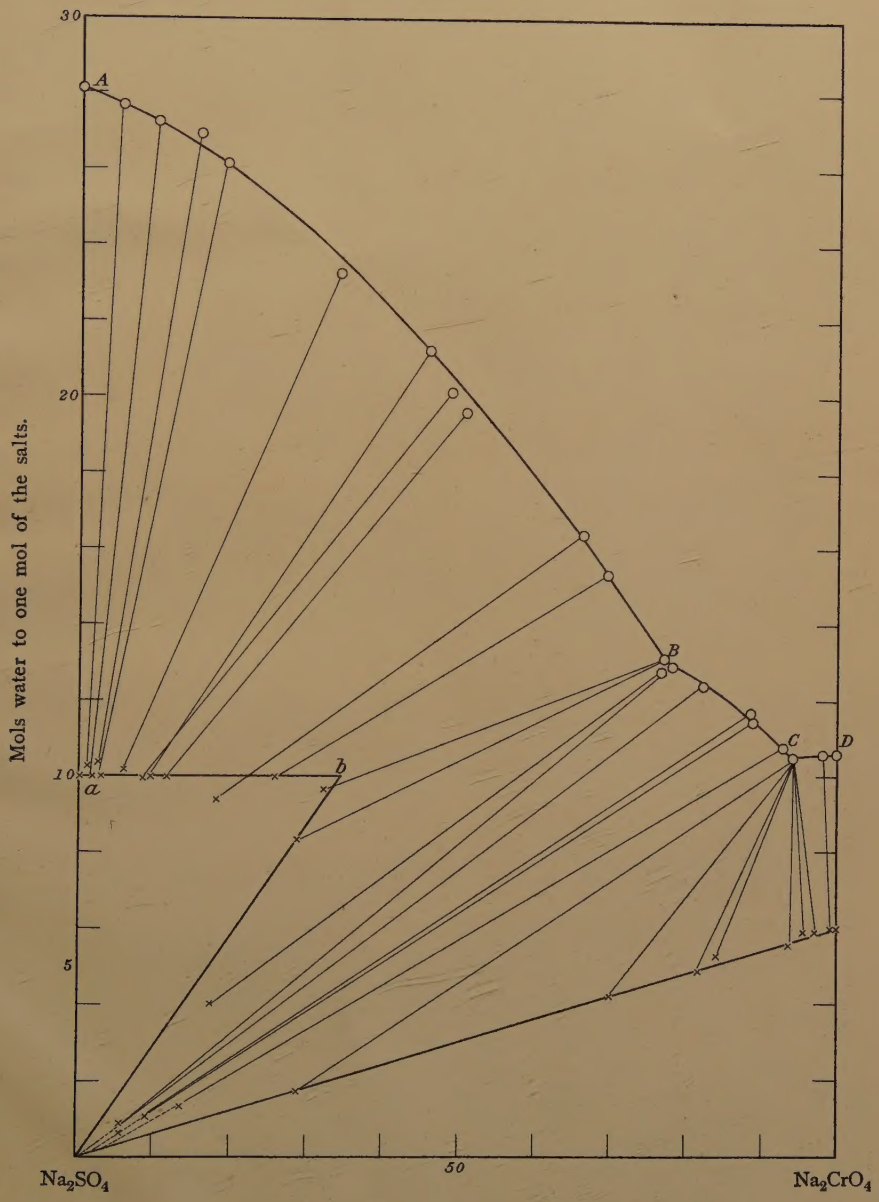


Fig. 2.

Temperature : 25.°0



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